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A NOTE ON THE ABNORMAL MAGNETIC BEHAVIOUR OF A TETRAHEDRAL COPPER (II) COMPOUND AT LOW TEMPERATURE

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In a previous publication (Bose, Lahiry and Ghosh 1965) we derived the ligand field theory of a flattened tetrahedral copper (II) compound Cs_2CuCl_4, where the complex anion $[CuCl_4]^{2-}$ has the symmetry D_{2d} We now report the preliminary magnetic studies on a few more tetrahedral coppper (II) compounds of the general formula $M_2^I[CuX_4]$ (where, M^I = Cs or $(CH_3)_4N$; X = Cl or Br) The compounds $[(CH_3)_4N]_2CuCl_4$ and Cs_2CuBr_4 have been shown from X-ray analysis (Morosin and Lingafelter, 1960) to belong to the space group Pnma, and the coordination tetrahedron is flattened along one of the symmetry axis, S_4. The other compound $[(CH_3)_4N]_2[CuBr_4]$ (Morsin and Lawson, 1964) is isomorphous with the others but its complete structural data are not yet available.

The principal crystalline anisotropies and the mean susceptibilities of these compounds have been measured by the method of Guha Thakurata *et al* (1966) and of Bose *et al* (1963) respectively, at a large number of temperatures in the range 300°K to 68°K. Assuming uniaxial symmetry the ionic anisotropies can be calculated from the relation

$$K_{\parallel}-K_{\perp}=\frac{\chi_c-\chi_a}{\gamma^2-\alpha^2}=\frac{\chi_a-\chi_b}{\alpha^2-\beta^2}=\frac{\chi_c-\chi_b}{\gamma^2-\beta^2}, \qquad \ldots (1)$$

where α, β, γ are the direction cosines of the symmetry axis (S_4) of the complex anion with respect to the a, b, c axes of the crystal. However, the ionic anisotropy in this case can be more simply calculated using the equation $K_{\parallel}-K_{\perp}=(\chi_c-\chi_b)+(\chi_a-\chi_b)$ since β has been found to be zero from X-ray results of the three compounds, so that with only two principal magnetic anisotropy measurements we can determine the value and the sign of $(K_{\parallel}-K_{\perp})$without recourse to the values of the direction cosines obtained from X-ray data For example, we can determine the ionic anisotropy of the compound $[N(CH_3)_4]_2[CuBr_4]$ whose detailed X-ray structure has not yet been reported. The values of the direction cosines calculated in this manner for the above compound at room temperature are found to

be close to those of the other isomorphous ones mentioned earlier. Further, we can determine the orientation of the ionic axes with respect to the crystallographic axes at all temperatures from the anisotropy measurements only. It may be seen that there is no direct relation of the relative magnitudes of $K_{\parallel}$ and $K_{\perp}$ with the elongation or flattening of the tetrahedron.

This particular compound showed some magnetic anomaly at about 238°K in sharp contrast to the others. From 300°K down to just above 238°K, with the crystal suspended in the magnetic field about "b" axis, the value of $(\chi_c - \chi_a)$ increased from 110.6 to 161.5 units and "c" axis was along the direction of the magnetic field. At 238°K the crystal sharply rotated in the horizontal plane through 90° so that the "a" axis was then along the field and the value of the principal anisotropy i.e. $(\chi_a - \chi_c)$, was found to be 80 units. The setting direction did not change any further on cooling down to 68°K. The above change was very sharp and has been found to be reversible with respect to temperature. The thermal variation of the other two principal anisotropies i.e. $(\chi_c - \chi_b)$ and $(\chi_a - \chi_b)$ also showed some peculiarities at the same temperature 238°K, though no change in the setting direction of the corresponding suspensions along "a" axis or "c" axis was noted for either (Fig. 1). It is therefore probable that the

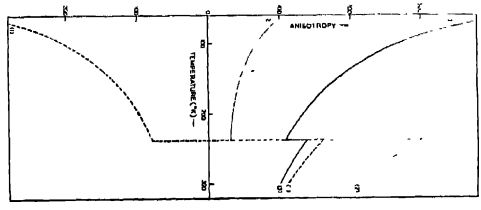

Fig. 1., Principal Crystalline Anisotropies
(1) $(\chi_a - \chi_c) \times 10^6$, (2) $(\chi_b - \chi_c) \times 10^6$ (3) $(\chi_a - \chi_b) \times 10^6$
v. s. Temperature (°K) curves of $[N(CH_3)_4]_2\ CuBr_4$.

sudden reversal of the principal magnetic axes in magnitude is not accompanied by a crystallographic change from orthorhombic system, unless the change over is pseudo-orthorhombic in character. Again, if the $K_{\parallel}$ axis, i.e., the symmetry axis undergoes rotation with decreasing temperature so that the angles subtended by the $K_{\parallel}$ axis with the crystallographic "c" and "a" axes respectively change with temperature and cross the value of $\pi/4$ at about 238°K, then it is easy to show from eqn. (1) that the setting direction will change by $\pi/2$ and $K_{\perp}$ will be greater than $K_{\parallel}$. But the angles, made by $K_{\parallel}$ axis lying in ac plane with the "c" axis in the temperature range 300°K to 238°K, calculated using the experimental values of anisotropy and eqn. (1), have been found to lie between 34°39′ to 34°6′ thus precluding this possibility decisively. The value of the mean susceptibility of this compound was found to remain constant in the temperature region of

240°K to 230°K (Fig. 2). Although at room temperature no detailed X-ray results have been reported as yet, preliminary X-ray study at low temperature carried out in this laboratory showed a marked change in the intensity of spots which may be correlated to shifts in the co-ordinates of some heavy atoms, probably the ligand Br atoms. But we cannot say at this stage, whether the space group of the crystal, or the symmetry of the complex anion undergoes change below 238°K. We are waiting for more detailed X-ray data to elucidate the nature of this change.

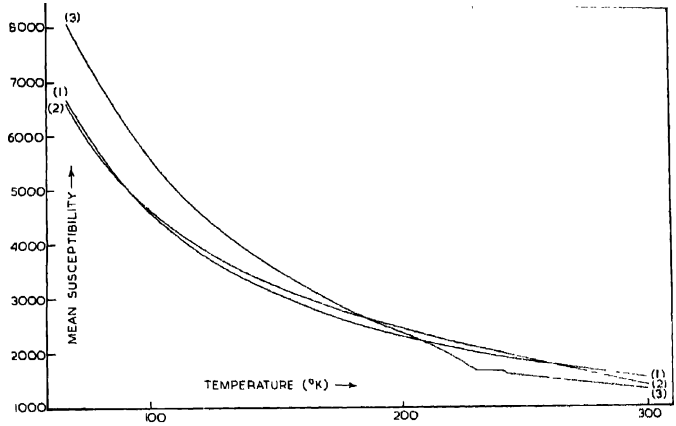

Fig 2. Mean Gram Ionic Susceptibility $\bar{\chi}_A \times 10^6$. v. s Temperature (°K) of (1) $[N(CH_3)_4]_2\,CuCl_4$. (2) $Cs_2\,CuBr_4$. (3) $[N(CH_3)_4]_2CuBr_4$

Measurements of anisotropy and mean magnetic moments of the compounds $[(CH_3)_4N]_2\,[CuCl_4]$ and Cs_2CuBr_4 did not show any abnormal magnetic behaviour with variation of temperature. However, the ionic anisotropies at 300°K as well as at 68°K for the first compound are found to be small compared to the second compound. These aspects will be discussed in details in a future paper.

Polarised crystal spectra of Cs_2CuBr_4 (Karipides and Piper, 1962) at 77°K and of $[(CH_3)_4N]_2\,[CuBr_4]$ in organic solvents (Furlani and Morpugo, 1963) indicates the presence of an orbital singlet $^2B_2$ to lie lowest and a doublet ^2E separated by about 5000 cm^{-1} above the singlet. Paramagnetic resonance measurements at 77°K of $[(CH_3)_4N]_2\,[CuCl_4]$ in $[ZnCl_4]^{2-}$ (Sharnoff and Reimann, 1965) give the approximately axial g-values as $g_{\parallel} = 2.462$, and $g_{\perp} = (2.078, 2.101)$. No resonance data are yet available for the other two. We have observed resonance signals for $[(CH_3)_4N]_2[CuBr_4]$ at low temperatures in our laboratory which will be of great help in the further analysis. A preliminary attempt to correlate magne-

tic anisotropy, mean susceptibility and g-values, where available, appears to indicate a lowest lying orbital singlet $^2B_2$, including the effects of the anisotropic orbital reduction factor and S--O reduction factors.

Full details of the theory and experimental results for these compounds will be published in due course. The authors express their gratitude to Prof. A. Bose, D.Sc., F.N.I. for helpful criticism and advice.

REFERENCES

Bose, A., Dutta Roy, S K., Ghosh, P K. and Mitra, S., 1963, *Indian J. Physics*, **37**, 505.

Bose, A., Lahiry, S. and Ghosh U. S., 1965, *J. Phys. Chem. Solids*, **26**, 1747.

Guha Thakurta, D and Mukhopadhyay, D., 1966, *Indian J. Physics*, **40**, 69.

Furlani, C., and Morpugo, G., 1963, *Theo Chem Acta*, **1**, 102.

Karipides, A. G and Piper, T S., 1962, *Inorg Chem.*, **1**, 970

Morosin, B., and Lingafelter, E. C., 1961, *J. Phys. Chem*, **65**, 50

———————————————, 1960, *Acta, Cryst*, **13**, 807

Morosin, B. and Lawson, K., 1964, *J Mol Spectroscopy*, **12**, 98

Sharnoff, M and Reimann, C. W., 1965, *J. Chem Phys*, **43**, 2993